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(54) Title: PARTICULATE TITANIUM DIOXIDE COATED PRODUCT AND METHOD OF FORMING TITANIUM DIOXIDE COATED PARTICLES

(57) Abstract: A composition of matter comprises particles each having a substrate being an oxide or other suitable compound of a metal other than titanium or of certain non-metal elements, and a coating on said substrate being a layer of titanium dioxide. A method of forming particles of titania-coated substrate, includes contacting a bed of hydrated particles of an oxide or other suitable compound of a metal other than titanium or of certain non-metal elements with a fluid medium containing flowing titanium tetrachloride, under conditions in which a layer comprising one or more involatile oxychloride or oxide compounds is formed at and below the surface of each of a multiplicity of the particles of the oxide or other suitable compound which thereby provides a substrate for the layer. The oxychloride or oxide compound or compounds are treated to convert the layer to a titania coating on the particles.

## PARTICULATE TITANIUM DIOXIDE COATED PRODUCT AND METHOD OF FORMING TITANIUM DIOXIDE COATED PARTICLES

**Field of the Invention**

This invention relates to a commercially usable product containing titanium  
5 dioxide ( $\text{TiO}_2$ ), also known as titania, and to methods for its production that are generally applicable to forming coated particles. In a particular embodiment, the invention provides a product which may be a substitute for conventional pigment grade  $\text{TiO}_2$ , currently the white base pigment used in most paint products, in plastics and paper and in many other applications.

10

**Background Art**

There are two principal technologies for producing pigment-grade titanium  
dioxide. The more recent is the Chloride Process in which titanium tetrachloride  
( $\text{TiCl}_4$ ), produced by chlorination of synthetic rutile, is reacted with oxygen at about  
1000°C to give  $\text{TiO}_2$  in the rutile crystal form that is normally required for use as a  
15 pigment. In the older Sulphate Process ilmenite is treated with sulphuric acid to give titanyl sulphate ( $\text{TiOSO}_4$ ) which is hydrolysed to  $\text{TiO}_2$  in the anatase form. The anatase form must then be calcined to rutile at about 1000°C. The products from both processes are subjected to various proprietary finishing steps for ultimate use as pigments.

20

In the prior art, powders have been proposed in which mixtures of  
components include alumina and titania and which are applied by flame spraying  
to steel and other substrates to provide coatings that are highly impervious and  
abrasion, corrosion and oxidation resistant. For example, US patent 3607343  
discloses a wide range of spray powders which include complex mixtures of many  
25 oxides, including alumina and titania, as well as fluxing ceramics such as lithium cobaltite and thermally unstable resin varnishes. The mixed powders are applied through a high temperature spray gun to produce a continuous grey or black layer on a metal substrate. These coatings differ totally from conventional titania based pigments and from the titania coated alumina proposed here. The former are very

fine white powders comprising only pure titania, while the latter is a fine white powder of alumina particles coated with titania.

### Summary of the Invention

In a first aspect, a fundamental concept of this invention is to provide an  
5 alternative pigment-grade titanium material in which the particles are not solid  
titania but instead a titania-coated substrate of a suitable material such as a metal  
oxide. Moreover, in a preferred form, the invention entails the further concept of  
producing the titania-coated alumina from intermediates of the aforementioned  
Chloride Process and of the well known Bayer Process for producing alumina from  
10 bauxite ore. This production technique has broader application to the formation of  
coated particles.

The present invention in its most general form provides, in its first aspect, a  
composition of matter comprising particles each having a substrate being an oxide  
or other suitable compound of a metal other than titanium or of certain non-metal  
15 elements, and a coating on said substrate being a layer of titanium dioxide. The  
titania coating may be a uniform, substantially homogenous undivided layer of  
titanium dioxide onto and into the underlying substrate or alternatively it may be  
randomly available over and into the surface of the substrate. The coating is  
preferably effected in a simple hydrolysis reaction.

20 In a second aspect, the invention provides a method of forming particles of  
titania-coated substrate, including :

contacting a bed of hydrated particles of an oxide or other suitable  
compound of a metal other than titanium or of certain non-metal elements  
with a fluid medium containing flowing titanium tetrachloride, under  
25 conditions in which a layer comprising one or more involatile oxychloride or  
oxide compounds is formed at and below the surface of each of a  
multiplicity of said particles of said oxide or other suitable compound which  
thereby provides a substrate for said layer; and

treating said oxychloride or oxide compound or compounds to convert the layer to a titania coating, preferably a pigment grade coating, on the particles.

More generally, in a third aspect, the invention provides a method of  
5 forming particles having a metal oxide coating on a substrate, including :

contacting a bed of hydrated particles of an oxide or other suitable compound of a first metal or of certain non-metal elements with a fluid medium containing a halide of a second metal, under conditions in which a layer comprising one or more involatile oxyhalide or oxide compounds of  
10 the second metal is formed at and below the surface of each of a multiplicity of said particles of said oxide or other suitable compound which thereby provides a substrate for said layer; and

treating said oxyhalide or oxide compound or compounds to convert the layer to a coating of an oxide of said second metal.

15 The preferred halide in the third aspect of the invention is chloride, whereby the involatile oxyhalide compound(s) is an oxychloride compound.

In any advantageous application of said third aspect, the second metal is titanium whereby said coating is a titania coating.

### **Further Preferred Aspects of the Invention**

20 The bed of hydrated particles is preferably a moving bed.

In all of the first, second and third aspects, the oxide or other compound is advantageously selected for its ability to absorb or adsorb sufficient water to sustain the formation of said layer.

In the first and second aspects, the substrate is preferably substantially less  
25 valuable or expensive than titania. A suitable oxide for the substrate is alumina,

but more generally the hydrated particles may be selected from the group including oxides and hydroxides of aluminium, silicon, zinc, lead, tin, bismuth, and other transition metal, group III and group IV elements. Some carbonates and other compounds may also be suitable as substrates. These include carbonates  
5 of calcium and magnesium and of the elements listed above as providing suitable oxide substrates.

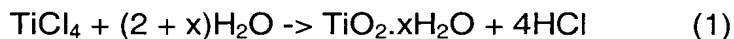
The titania coating on each particle preferably includes a lowermost transition zone in which titania is interspersed into the underlying substrate.

Where the hydrated metal oxide particles are hydrated alumina particles,  
10 these may comprise or include aluminium hydroxide  $\text{Al}(\text{OH})_3$ , also known as alumina trihydrate or gibbsite, or aluminium oxide hydroxide  $\text{AlO}.\text{OH}$ , also known as aluminium monohydroxide or boehmite, but can be any suitable form that provides sufficient hydroxyl groups for the formation of the titanium oxychloride compounds. It is believed that the titanium tetrachloride ( $\text{TiCl}_4$ ) reacts with the  
15 hydroxyl groups on the surface of the hydrated alumina particles to produce the titanium oxychloride compounds.

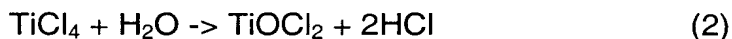
If, on the other hand, reaction of  $\text{TiCl}_4$  with the hydroxyl groups of the hydrated alumina or other substrate is insufficient, the extent of reaction can be increased by pretreating the hydrated alumina or other substrate with steam or  
20 water to ensure an appropriate amount of water, absorbed on the alumina, available for a more extended hydrolysis reaction.

The aforesaid conditions preferably include a proportional presence of water which is in deficit relative to the alternative reaction of the titanium tetrachloride to produce hydrated titania and an aqueous solution of hydrochloric  
25 acid as in reaction (1).

$\text{TiCl}_4$  is a volatile liquid (mp  $-23^\circ\text{C}$ , bp  $137^\circ\text{C}$ ) which is very readily hydrolysed. With excess water, the overall reaction produces hydrated titania ( $\text{TiO}_2.x\text{H}_2\text{O}$ ) and an aqueous solution of hydrochloric acid according to the following equation :



Reaction of  $\text{TiCl}_4$  with a deficit of water, on the other hand, leads to the formation of relatively involatile oxychlorides of titanium, of which the best characterised is titanium oxydichloride ( $\text{TiOCl}_2$ ), in accordance with the following equation :



In one embodiment of the second aspect of the invention, which might be referred to as Solvent Phase Hydrolysis, the fluid medium is a solution of  $\text{TiCl}_4$  in an organic solvent. The organic solvent is preferably one which is non-polar and immiscible with water, such as carbon tetrachloride, benzene or cyclohexane, or of very low polarity such as toluene, trichlorethylene, or a hydrocarbon such as heptane.  $\text{TiCl}_4$  is reported as being very soluble in non-polar solvents while  $\text{TiOCl}_2$ , the typical product of reaction formed at the interface, is reported as being sparingly soluble in non-polar solvents. A more polar solvent, such as an alcohol or a ketone, may be more efficient in wetting the solid hydrated alumina, but  $\text{TiOCl}_2$  is likely to be soluble in such a solvent and to diffuse away from the surface of the solid.

When the  $\text{TiCl}_4$  reacts with the hydrated alumina an oxychloride such as  $\text{TiOCl}_2$  will be formed at the surface of the alumina as indicated in equation (2) and the  $\text{HCl}$  also formed is soluble in non-polar solvents and, for recycling of the solvent, could be stripped from the solvent by distillation or by extraction with an aqueous alkaline solution in the case of a water-immiscible solvent. An oxychloride of aluminium, such as  $\text{AlOCl}$ , is also likely to be formed in the reaction interface.

The contacting step may be carried out at ambient temperature. If necessary, the extent of equation (2) could be increased by reacting the  $\text{TiCl}_4$  solution under reflux additions, or at some appropriate temperature above ambient.

One alternative form of said treatment of the titanium oxychloride layer may be a hydrolysis treatment in which the titanium oxydichloride coated hydrated alumina is treated with steam under conditions that result in the coating of the alumina with hydrated titanium ( $\text{TiO}_2 \cdot x\text{H}_2\text{O}$ ) in accordance with the following  
5 reaction:



HCl, the other product of this reaction, is very volatile and is swept away from the reaction zone.

When the hydrated alumina, coated with  $\text{TiOCl}_2$  and a compound such as  
10  $\text{AlOCl}$ , is heated through temperatures of 200 to 400°C, the  $\text{TiOCl}_2$  and  $\text{AlOCl}$  are converted in a pyrohydrolysis reaction with excess water vapour to give a mixed zone of  $\text{AlO} \cdot \text{OH}$  and  $\text{TiO}(\text{OH})_2$  which bonds the  $\text{TiO}_2$  formed after calcination at high temperatures to the  $\text{Al}_2\text{O}_3$  substrate. At temperatures of about 1000°C, the hydrated titania is calcined to the usually required pigment-grade rutile form of  
15  $\text{TiO}_2$ . If anatase coating is required, the final calcination should be conducted at temperatures considerably less than 1000°C, for example at temperatures of about 400°C to 800°C.

If a less thermally stable substrate such as calcium carbonate is used, calcination at a temperature lower than 1000°C, for example 400°C to 800°C, may  
20 be necessary to prevent conversion of the calcium carbonate to strongly basic calcium oxide. Under these conditions, the titania coating would be in the anatase form.

Alternatively, the pyrohydrolysis reaction can be conducted as a separate step before calcination.

25 In an alternative embodiment of the treatment of the titanium oxychloride layer, the coated alumina particles may be subjected to moderate heating (eg. to a temperature in the range 150 to 250°C, preferably above 180°C), in a gas stream under conditions whereby the oxychlorides decompose to titanium dioxide and

titanium tetrachloride as follows :-



The  $\text{TiO}_2$  remains as a coating of the surface of the alumina and the latter, a volatile gas, is swept away and recycled. If the resulting  $\text{TiO}_2$  is in the anatase form, it must be calcined to obtain pigment-grade rutile.

The heating and calcination steps may be combined. In such a case, the initial titanium oxychloride-coated alumina is preferably heated to a temperature of about  $1000^\circ\text{C}$  to effect the calcination to rutile and to remove any residual titanium tetrachloride.

In another embodiment of the second aspect of the invention, known as Vapour Phase Hydrolysis, the fluid medium containing flowing titanium tetrachloride is a gas stream containing titanium tetrachloride. The gas stream preferably includes titanium tetrachloride ( $\text{TiCl}_4$ ) in dry air or nitrogen.

When the  $\text{TiCl}_4$  reacts with the hydrated alumina, the layer comprising one or more titanium oxychloride compounds, involatile in this embodiment, may include primarily titanium oxydichloride ( $\text{TiOCl}_2$ ), as in equation (2).

Preferably, the contacting step is carried out at ambient temperature whereby the other product of equation (2),  $\text{HCl}$ , is removed in the gas stream.

If necessary, the extent of reaction (2) can be controlled by adjustment of the  $\text{TiCl}_4$  contribution in the gas stream by increasing the temperature and the vapour pressure of the  $\text{TiCl}_4$  source, or by increasing the temperature of the alumina reaction bed.

It is current commercial practice to coat titanium dioxide particles with thin layers of oxides of elements such as silicon, aluminium and zirconium or combinations of such oxides in order to improve physical properties such as dispersibility, and to minimise interaction of the titanium dioxide particles with



ultra-violet light. It will be appreciated that the novel technology described in this specification for coating an oxide or other substrate with titania can be used to coat the titania-coated oxide or other substrate with oxides of silicon, aluminium or zirconium or with combinations of such oxides by exposing the hydrated titanium  
5 oxychloride coated particles to solutions of appropriate concentrations in solvents of zero or very low polarity of suitable halides of silicon, aluminium and zirconium or any combination of such halides. Preferred halides include silicon tetrachloride, aluminium chloride and zirconium chloride or any combination of those or other chlorides. Subsequent pyrohydrolysis reactions, conducted separately or in situ  
10 during calcination, would provide particles of the substrate coated firstly with titania and then with oxides such as silica, alumina or zirconia or combinations of such oxides.

An alternative approach is to pyrohydrolyze the particles coated with titanium oxychloride, hydrate them again and then react those particles  
15 suspended in cyclohexane with silicon or other chloride, and then pyrohydrolyze and calcine the product.

It will be appreciated that, given the relative price differential between alumina and pigment-grade titanium dioxide, the proposed composition of the invention would be economically attractive as a pigment product. If the material is  
20 used for this purpose, the initial alumina feed particles would typically need to be pretreated, eg. by milling, so that the final coated particles are of dimensions consistent with use as a pigment grade powder.

It will also be appreciated that the production process is attractive because the components utilised can be intermediates, respectively titanium tetrachloride and hydrated alumina, in the commercially established Chloride Process in the  
25  $\text{TiO}_2$  industry and in the Bayer Process in the alumina industry. Hydrated alumina is already established as a starting material for various aluminium chemicals and, after calcination and grinding, itself has applications in ceramics and as a wear resistant constituent in other materials. In fact it is reasonable to assume that the  
30 product of the invention may be used as feedstock to produce an aluminium-titanium metal alloy.

### Example 1

Aluminium hydroxide,  $\text{Al}(\text{OH})_3$ , was hydrated by adding  $\text{H}_2\text{O}$  dropwise to a vigorously stirred suspension of 300g of  $\text{Al}(\text{OH})_3$  in  $\text{CCl}_4$ . The solid was isolated by vacuum filtration, washed with  $\text{CCl}_4$  and air-dried. The weight of the solid indicated  
5 that 73 mol % of water had been adsorbed. The  $\text{TiCl}_4$  (10 mol %) was added dropwise to a suspension of 30 grams of the hydrated  $\text{Al}(\text{OH})_3$  in 100ml of  $\text{CCl}_4$ . The  $\text{Al}(\text{OH})_3$  assumed a yellow colour, that of  $\text{TiOCl}_2$ , immediately. After 1 hour, a 1ml aliquot of  $\text{CCl}_4$  was taken and syringed into an aqueous solution of  $\text{NaOH}$ . No precipitate of insoluble  $\text{TiO}_2$  was observed indicating that the reaction was  
10 complete. Part of the solid product was analysed using X-ray fluorescence techniques. The initial solid contained 56.3%  $\text{Al}_2\text{O}_3$ , 8.2%  $\text{TiO}_2$  and 6.9% Cl and other minor constituents, indicating the presence of  $\text{TiOCl}_2$ . After heating to 1000°C, XRF analysis showed 89.1%  $\text{Al}_2\text{O}_3$ , 12.6%  $\text{TiO}_2$  and 0.03% Cl. X-ray diffraction analysis showed that, after heating to 200°C the solid was mainly  
15 gibbsite,  $\text{Al}(\text{OH})_3$ , with a small amount of boehmite,  $\text{AlO.OH}$ . Boehmite was the dominant phase at 400°C while, after heating to 600°C and 800°C, the principal phases were anatase ( $\text{TiO}_2$ ) and delta- $\text{Al}_2\text{O}_3$ . After ignition to 1000°C, the phases present were rutile ( $\text{TiO}_2$ ) and corundum (alpha- $\text{Al}_2\text{O}_3$ ). This is consistent with the formation of non-crystalline anatase with gibbsite and boehmite at temperatures  
20 up to about 600°C with crystalline anatase undergoing a phase change at temperatures approaching 1000°C to produce a 10 to 12% coating of rutile.

### Example 2

Gibbsite,  $\text{Al}(\text{OH})_3$ , was subjected to wet grinding to produce particles with an average size of about 1 micron. The suspension was filtered. 11.2g of the wet  
25 filter cake (water content about 50 mol %) was stirred as a suspension in 100ml of cyclohexane and 1.4ml of  $\text{TiCl}_4$  (about 10 mol %) was added dropwise and slowly by syringe. XRF analysis showed that the solid residue recovered after filtration contained 48.40%  $\text{Al}_2\text{O}_3$ , 13.10%  $\text{TiO}_2$  and 8.24% Cl. Calcination of this residue at 1000°C provided a solid with 76.8%  $\text{Al}_2\text{O}_3$ , 20.50%  $\text{TiO}_2$  and 0.06% Cl. IFESSEM  
30 investigation showed that the majority of the  $\text{Al}_2\text{O}_3$  particles that reacted were totally covered with  $\text{TiO}_2$  with some titania impregnating the particles.

**Example 3**

10g of  $\text{CaCO}_3$  was vigorously stirred in 100ml cyclohexane and water (0.9ml, 50 mol %) was added by syringe.  $\text{TiCl}_4$  was added as in examples 1 and 2 and the resulting solid recovered by filtration. XRF analysis showed that it  
5 contained 49.4%  $\text{CaO}$ , 8.9%  $\text{TiO}_2$  and 7.97%  $\text{Cl}$ .

**CLAIMS**

- 1 A composition of matter comprising particles each having a substrate being  
an oxide or other suitable compound of a metal other than titanium or of  
certain non-metal elements, and a coating on said substrate being a layer  
5 of titanium dioxide.
- 2 A composition of matter according to claim 1 wherein said layer is a  
uniform, substantially homogenous undivided layer of titanium dioxide.
- 3 A composition of matter according to claim 1 wherein said layer is randomly  
distributed over and into the surface of the substrate.
- 10 4 A composition of matter according to claim 1, 2 or 3 wherein said oxide or  
other compound is selected for its ability to absorb or adsorb sufficient  
water to sustain the formation of said layer.
- 5 A composition of matter according to any preceding claim, wherein said  
substrate is substantially less valuable or expensive than titania.
- 15 6 A composition of matter according to any one of claims 1 to 5 wherein said  
substrate is alumina.
- 7 A composition of matter according to any one of claims 1 to 5 wherein said  
substrate is selected from the group consisting of oxides, hydroxides and  
carbonates of aluminium, silicon, zinc, lead, tin, bismuth, and other  
20 transition metal, group III and group IV elements, and carbonates of  
calcium and magnesium.
- 8 A composition of matter according to any preceding claim wherein said  
coating of titanium dioxide on each particle includes a lowermost transition  
zone in which titanium dioxide is interspersed into the underlying substrate.
- 25 9 A composition of matter according to any preceding claim further including

an outer coating on said titanium dioxide layer of a substance to minimise interaction of the titanium dioxide layer with incident ultraviolet light.

- 10     A method of forming particles of titania-coated substrate, including :
- 5     contacting a bed of hydrated particles of an oxide or other suitable compound of a metal other than titanium or of certain non-metal elements with a fluid medium containing flowing titanium tetrachloride, under conditions in which a layer comprising one or more involatile oxychloride or oxide compounds is formed at and below the surface of each of a multiplicity of said particles of said oxide or other suitable compound which
- 10     thereby provides a substrate for said layer; and
- treating said oxychloride or oxide compound or compounds to convert the layer to a titania coating, on the particles.
- 11     A method according to claim 10, wherein said coating is a pigment grade coating.
- 15     12     A method according to claim 10 or 9 wherein said bed of hydrated particles is a moving bed.
- 13     A method according to claim 10, 11 or 12 wherein said oxide or other compound is selected for its ability to absorb or adsorb sufficient water to sustain the formation of said layer.
- 20     14     A method according to any one of claims 10 to 13, wherein said substrate is substantially less valuable or expensive than titania.
- 15     A method according to any one of claims 10 to 15 wherein said coating of titanium dioxide on each particle includes a lowermost transition zone in which titanium dioxide is interspersed into the underlying substrate.
- 25     16     A method according to any one of claims 10 to 15 wherein said hydrated

particles are selected from the group consisting of oxides, hydroxides and carbonates of aluminium, silicon, zinc, lead, tin, bismuth, and other transition metal, group III and group IV elements, and carbonates of calcium and magnesium.

- 5 17 A method according to any one of claims 10 to 15 wherein said hydrated particles are alumina particles.
- 18 A method according to claim 17 wherein said titanium tetrachloride ( $\text{TiCl}_4$ ) reacts with the hydroxyl groups or water molecules on the surface of the hydrated alumina particles to produce the titanium oxychloride compounds.
- 10 19 A method to claim 17 or 18 wherein said hydrated alumina particles comprise or include aluminium hydroxide  $\text{Al}(\text{OH})_3$ , also known as alumina trihydrate or gibbsite, or aluminium oxide hydroxide  $\text{AlO}.\text{OH}$ , also known as aluminium monohydroxide or boehmite.
- 20 A method according to any one of claims 10 to 19, further including  
15 pretreating the hydrated alumina or other substrate with steam or water to ensure an appropriate amount of water, absorbed on the substrate, available for a more extended hydrolysis reaction.
- 21 A method according to any of claims 10 to 20 wherein said aforesaid  
20 conditions include a proportional presence of water which is in deficit relative to the alternative reaction of the titanium tetrachloride to produce hydrated titania and an aqueous solution of hydrochloric acid.
- 22 A method according to any one of claims 10 to 21 wherein the fluid medium is a solution of  $\text{TiCl}_4$  in an organic solvent.
- 23 A method according to claim 22, wherein said organic solvent is one which  
25 is non-polar or of very low polarity, and immiscible with water.
- 24 A method according to claim 23, wherein said organic solvent is selected

from the group consisting of carbon tetrachloride, benzene, cyclohexane, toluene, trichlorethylene, and heptane.

- 25 A method according to any one of claims 10 to 24, including a hydrolysis  
5 treatment in which the titanium oxydichloride coating is treated with steam  
under conditions that result in the coating of the substrate with hydrated  
titanium ( $\text{TiO}_2 \cdot x\text{H}_2\text{O}$ ).
- 26 A method according to any one of claims 10 to 25, wherein said treating  
step includes calcination at a temperature in the range  $200^\circ\text{C}$  to  $1000^\circ\text{C}$ .
- 10 27 A method according to any one of claims 10 to 25, wherein the coated  
particles are subjected to moderate heating in a gas stream under  
conditions whereby the oxychlorides decompose to titanium dioxide and  
titanium tetrachloride, and the  $\text{TiO}_2$  remains as a coating of the surface of  
the substrate and titanium tetrachloride is swept away and recycled.
- 15 28 A method according to any one of claims 10 to 21, wherein the fluid  
medium containing flowing titanium tetrachloride is a gas stream containing  
titanium tetrachloride.
- 29 A method according to any one of claims 10 to 28 further including an outer  
coating on said titanium dioxide layer of a substance to minimise interaction  
of the titanium dioxide layer with incident ultraviolet light.
- 20 30 A method of forming particles having a metal oxide coating on a substrate,  
including :
- 25 contacting a bed of hydrated particles of an oxide or other suitable  
compound of a first metal or of certain non-metal elements with a fluid  
medium containing a halide of a second metal, under conditions in which a  
layer comprising one or more involatile oxyhalide or oxide compounds of  
the second metal is formed at and below the surface of each of a  
multiplicity of said particles of said oxide or other suitable compound which

thereby provides a substrate for said layer; and

treating said oxyhalide or oxide compound or compounds to convert the layer to a coating of an oxide of said second metal.

- 31 A method according to claim 30 wherein said bed of hydrated particles is a  
5 moving bed.
- 32 A method according to claim 30 or 31 wherein said oxide or other  
compound is selected for its ability to absorb or adsorb sufficient water to  
sustain the formation of said layer.
- 33 A method according to claim 30, 31 or 32 wherein said hydrated particles  
10 are selected from the group consisting of oxides, hydroxides and  
carbonates of aluminium, silicon, zinc, lead, tin, bismuth, and other  
transition metal, group III and group IV elements, and carbonates of  
calcium and magnesium.
- 34 A method according to any one of claims 30 to 33 wherein said halide  
15 reacts with the hydroxyl groups or water molecules on the surface of the  
hydrated particles to produce the oxyhalide compounds.
- 35 A method according to any one of claims 30 to 34 wherein the fluid medium  
is a solution of a halide in an organic solvent.
- 36 A method according to claim 35, wherein said organic solvent is one which  
20 is non-polar or of very low polarity, and immiscible with water.
- 37 A method according to claim 36, wherein said organic solvent is selected  
from the group consisting of carbon tetrachloride, benzene cyclohexane,  
toluene, trichlorethylene, and heptane.
- 38 A method according to any one of claims 30 to 37 wherein said halide is a  
25 chloride, whereby the or each oxyhalide compound is an oxychloride



compound.

- 39 A method according to claim 38 wherein said aforesaid conditions include a proportional presence of water which is in deficit relative to the alternative reaction of the chloride to produce a hydrated oxide and an aqueous solution of hydrochloric acid.
- 5
- 40 A method according to any one of claims 30 to 39 wherein said second metal is titanium whereby said coating is a titania coating.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU01/00272

**A. CLASSIFICATION OF SUBJECT MATTER**Int. Cl. <sup>7</sup>: C09C 1/00, 1/36, 3/06

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C09C 1/00, 1/36, 3/06

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Derwent WPAT and JAPIO  
Chemical Abstracts**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Derwent Abstracts Accession No. 93-025345/03, Class E32 I02 (E33), SU 1713886-A1 (Lengd. Lensovet. Techn. Inst.) 23 February 1992 (see entire abstract)	1, 5-7
X	Langmuir (1996), 12 (13), 3173-3179, "Titania Coatings on Monodisperse Silica Spheres (Characterization Using 2-Propanol Dehydration and TEM)", A. Hanprasopwattana <i>et al.</i> (see entire document, in particular page 3173, page 3174 (review of the previous literature (particularly references 12 and 14)), page 3178)	1-5, 7-8, 10, 13-16, 26, 28, 30, 32-34, 38, 40
X	Derwent Abstract Accession No. 97-532928/49, Class E32 G01, JP 09-255891 A (Yoshida Kogyo KK) 30 September 1997. (see entire abstract)	1-2, 5-7

☒ Further documents are listed in the continuation of Box C ☒ See patent family annex

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search  
27 March 2001

Date of mailing of the international search report

10 May 2001

Name and mailing address of the ISA/AU

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU01/00272

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Chemical Abstracts, volume 119, No. 22, issued 29 November 1993, Columbus, Ohio, USA, C. Deng <i>et al.</i> , "Preparation of titania/silica complex support by gas phase adsorption and dispersion state of molybdenum trioxide on the surface of complex support", page 635, column 1, the abstract No. 234888y, <i>Cuihua Xuebao</i> (1993), 14 (4), 281-286, (Chinese). (see the entire abstract)	1-3, 5, 7
X	Chemical Abstracts, volume 117, No. 4, issued 27 July 1992, Columbus, Ohio, USA, C. Deng <i>et al.</i> , "Preparation of titania/ $\gamma$ -alumina complex support by gas phase adsorption and state of titania on $\gamma$ -alumina surface", page 539 column 2 to page 540 column 1, the abstract No. 34416q, <i>Fenzi Cuihua</i> , (1992), 6 (1), 15-22, (Chinese). (see the entire abstract)	1-3, 5-7, 10, 14, 16-17, 25-26, 28, 30, 33-34, 38, 40
X	Chemical Abstracts, volume 116, No. 10, issued 9 March 1992, Columbus, Ohio, USA, L. I. Petrova <i>et al.</i> , "Phase formation and change of the surface acidity in synthesis of a titanium layer on $\gamma$ -alumina by molecular superposition", page 200, column 2, the abstract No. 86998e, <i>Zh. Prikl. Khim.</i> (Leningrad), (1991), 64 (7), 1435-1440, (Russian). (see the entire abstract)	1-7, 10, 13-14, 16-18, 28, 30, 32-34, 40
X	Chemical Abstracts, volume 121, No. 26, issued 26 December 1994, Columbus, Ohio, USA, Z. Wei and Q. Xin, "Studies of titania-alumina as support for molybdenum catalysts", page 229, column 1, the abstract No. 304322, <i>Wuli Huaxue Xuebao</i> , (1994), 10 (10), 931-935, (Chinese). (see the entire abstract)	1-7, 10, 13-14, 16-18, 28, 30, 32-34, 38, 40
X	Patent Abstracts of Japan, JP 60-099171 A (TITAN KOGYO KK) 3 June 1985 (see entire abstract)	1-2, 5, 7
X	Derwent Abstract Accession No. 98-562946/48, Class E33 G01 J04, JP 10-251016 A (Agency of Ind Sci & Technology) 22 September 1998 (see entire abstract)	1-2, 5, 7
X	Derwent Abstract Accession No. 89-215200/30, Class A93 L02 (A21 A26), HU T048660 A (Aluminiumipari Tervezo) 28 June 1989 (see entire abstract)	1-2, 5-7
X	Ind. Eng. Chem. Res. (1999), 38, 3381-3385, "Preparation of Heterogenous Photocatalyst (TiO <sub>2</sub> /Alumina) by Metallo-Organic Chemical Vapour Deposition", L. Lei <i>et al.</i> (see entire document, in particular page 3384 column 2)	1-2, 5-7

## INTERNATIONAL SEARCH REPORT

International application No.  
**PCT/AU01/00272**

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Inorganic Materials, (1995), <b>31</b> (2), 210-213, "Composition of the Sodium-Rich Surface Layer on Alumina and its Effects on Reaction with Ti Cl <sub>4</sub> and H <sub>2</sub> O Vapours", N. V. Dolgushev <i>et al.</i> (see page 210 column 2, page 212 column 2 and conclusion)	1-2, 4-8, 10, 13-18, 28, 30, 32-34, 38, 40
X	Journal of Chromatography, (1980), <b>189</b> , 139-144, "Liquid Chromatography on Metal Oxides with Silica Geometry", R. Aigner-Held and W. A. Aue (see page 140 lines 11-18, Table 1, page 142 lines 12-	1-2, 4-5, 7, 10, 13-14, 16, 28, 30, 32-34, 38, 40
X	GB 1480530 A (E. I. Du Pont De Nemours and Co) 20 July 1977 (see entire document, in particular page 2 lines 23-35, page 3 lines 21-30, page 6 line 28 to page 7 line 9, page 8 lines 18-22, page 8 line 53- page 9 line 38, examples 5-14, 16, 20 and 22-23).	1-2, 4-7, 10, 13-14, 16-19, 28, 30, 32-34, 40
X	EP 455401 A (Minnesota Mining and Manufacturing Co) 6 November 1991 (see entire document, in particular page 5 lines 47-50, page 6 line 12, page 9 lines 38-39)	1-2, 4, 7, 10, 12-13, 16, 28, 30-33, 40
X	US 5145719 A (Atsuya Towata and Mutsuo Sando) 8 September 1992 (see entire patent, in particular column 2 and examples 1-7	1-2, 4-7
X	US 5221341 A (K. Franz <i>et al.</i> ) 22 June 1993 (see entire patent, in particular column 1 line 51 to column 2 line 34 and column 4 lines 32-39)	1-2, 5, 7, 9
P,X	US 6063179 A (R. Schmid and N. Mronga) 16 May 2000 (see entire patent, in particular column 2 lines 45-50, column 3 lines 35-62 and column 5 line 4)	1-2, 5, 7, 9, 10-112, 14, 16, 28-31, 33, 40
P,X	US 6176918 A (R. Glausch <i>et al.</i> ) 23 January 2001 (see entire patent, in particular column 4 lines 33-38 and the examples)	1-2, 5, 9

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
**PCT/AU01/00272**

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report			Patent Family Member				
US	6176918	BR	9706758	CN	1205023	CZ	9801355
		DE	19639783	EP	888410	WO	9813426
US	6063179	DE	19614637	EP	892832	WO	9739066
US	5221341	CN	1068129	CZ	9201984	DE	4121352
		FI	922985	JP	5186705	MX	9203617
		EP	520313				
US	5145719	JP	4045835				
EP	455401	CA	2035294	JP	4230996	US	5156885
		US	5418062	US	5439705	US	5908698
		US	5593782				
GB	1480530	DE	2459118	FR	2278730	FR	2355855
		IT	1031045	IT	1123092	CA	1040779
		US	4187210	US	3950303	JP	50092337
HU	48660	NONE					
JP	10251016	NONE					
JP	9255891	NONE					
JP	4341342	NONE					
SU	1713886	NONE					
JP	60099171	NONE					

END OF ANNEX

**DERWENT-ACC-NO:** 2001-648297

**DERWENT-WEEK:** 200771

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**TITLE:** Pigment-grade titanium material for use as white pigment in, e.g., plastics, includes particles having titania-coated substrate of metal or non-metal oxide

**INVENTOR:** O'DONNELL T A; O'DONNELL T A ; PRICE D E

**PATENT-ASSIGNEE:** DEPCO TRH PTY LTD[DEPCN] , O'DONNELL T A[ODONI] , PRICE D E[PRICI]

**PRIORITY-DATA:** 2000AU-006194 (March 10, 2000)

**PATENT-FAMILY:**

<b>PUB-NO</b>	<b>PUB-DATE</b>	<b>LANGUAGE</b>
WO 0166652 A1	September 13, 2001	EN
AU 200140355 A	September 17, 2001	EN
EP 1280862 A1	February 5, 2003	EN
US 20030143421 A1	July 31, 2003	EN
AU 2001240355 B2	October 20, 2005	EN
US 7285328 B2	October 23, 2007	EN

**DESIGNATED-STATES :** AE AG AL AM AT AU AZ BA BB BG BR BY  
 BZ CA CH CN CO CR CU CZ DE DK DM DZ  
 EE ES FI GB GD GE GH GM HR HU ID IL  
 IN IS JP KE KG KP KR KZ LC LK LR LS  
 LT LU LV MA MD MG MK MN MW MX MZ NO  
 NZ PL PT RO RU SD SE SG SI SK S L TJ  
 TM TR TT TZ UA UG US UZ VN YU ZA ZW  
 AT BE CH CY DE DK EA ES FI FR GB GH  
 GM GR IE IT KE LS LU MC MW MZ NL OA  
 PT SD SE SL SZ TR TZ UG ZW AL AT BE  
 CH CY DE DK ES FI FR GB GR IE IT LI  
 LT LU LV MC MK NL PT RO SE SI TR

**APPLICATION-DATA:**

<b>PUB-NO</b>	<b>APPL-DESCRIPTOR</b>	<b>APPL-NO</b>	<b>APPL-DATE</b>
WO2001066652A1	N/A	2001WO- AU00272	March 13, 2001
AU 200140355A	N/A	2001AU- 040355	March 13, 2001
AU2001240355B2	N/A	2001AU- 240355	March 13, 2001
EP 1280862A1	N/A	2001EP- 911271	March 13, 2001
EP 1280862A1	N/A	2001WO- AU00272	March 13, 2001
US20030143421A1	N/A	2001WO- AU00272	March 13, 2001
US 7285328B2	N/A	2001WO- AU00272	March 13, 2001
US20030143421A1	N/A	2002US- 221436	December 3, 2002
US 7285328B2	Based on	2002US- 221436	December 3, 2002

**INT-CL-CURRENT :**

<b>TYPE</b>	<b>IPC DATE</b>
CIPP	B32B5/16 20060101
CIPS	B05D3/10 20060101
CIPS	B05D7/24 20060101
CIPS	C09C1/00 20060101
CIPS	C09C1/02 20060101
CIPS	C09C1/36 20060101
CIPS	C09C1/40 20060101
CIPS	C09C3/06 20060101

**ABSTRACTED-PUB-NO:** WO 0166652 A1

**BASIC-ABSTRACT:**

NOVELTY - Pigment-grade titanium material comprises particles having an oxide of a metal other than titanium or of certain non-metals as a substrate, and a layer of titanium dioxide as a coating on the substrate.

DESCRIPTION - An INDEPENDENT CLAIM is also included for a method of forming particles having a metal oxide coating on a substrate by contacting a bed of hydrated particles of an oxide of a first metal or of certain non-metals with a fluid medium containing a halide of a second metal, under conditions in which a layer comprising involatile oxyhalide or oxide compound(s) of the second metal is formed at and below the surface of each particle to provide a substrate for the layer; and treating the oxyhalide or oxide compound(s) to convert the layer to a coating of an oxide of the second metal.

USE - For use as white base pigment in paint products, in plastics and paper and other applications.

ADVANTAGE - The invention provides a substitute for conventional pigment grade titanium oxide.



**EQUIVALENT-ABSTRACTS:**

## INORGANIC CHEMISTRY

**Preferred Components:** The titania layer is uniform and homogeneously undivided or it is randomly distributed over and into the surface of the substrate. The oxide is selected for its ability to absorb or adsorb water to sustain the formation of the layer. The substrate is less valuable or expensive than titania. The coating of titanium dioxide on each particle includes a lowermost transition zone in which titanium dioxide is interspersed into the underlying substrate. An outer coating is on the titanium dioxide layer to minimize interaction of the layer with incident ultraviolet light.

**Preferred Materials:** The substrate is an oxide, hydroxide or carbonate of aluminum, silicon, zinc, lead, tin, bismuth, other transition metal, or group III or group IV element. It may also be a carbonate of calcium or magnesium. The bed of hydrated particles is a moving bed.

## ORGANIC CHEMISTRY

**Preferred Materials:** The fluid medium is a solution of a halide (preferably a chloride) in an organic solvent. The organic solvent is carbon tetrachloride, benzene cyclohexane, toluene, trichloroethylene, or heptane.

Gibbsite ( $\text{Al}(\text{OH})_3$ ) was subjected to wet grinding to produce particles with an average size of 1  $\mu\text{m}$ . The suspension was filtered. The filter cake was stirred as a suspension in cyclohexane (100 ml). Titanium tetrachloride (1.4 ml) was added dropwise. Analysis showed that the solid residue recovered after filtration contained 48.40% alumina ( $\text{Al}_2\text{O}_3$ ), 13.10% titania ( $\text{TiO}_2$ ), and 8.24% chloride. Calcination of this residue at 1000degreesC provided a solid with 76.8% alumina, 20.50% titania, and 0.06% chlorine. Scanning electron

microscopy investigation showed that the majority of the alumina particles that reacted were totally covered with titania with some titania impregnating the particles.

**TITLE-TERMS:** PIGMENT GRADE TITANIUM MATERIAL WHITE  
PLASTICS PARTICLE TITANIA COATING  
SUBSTRATE METAL NON OXIDE

**DERWENT-CLASS:** A60 F09 G01 G02 P42

**CPI-CODES:** A08-E02; A12-B01; F05-A06D; G01-A01; G01-A02; G01-A04; G01-A05; G01-A06; G01-A08; G01-A10; G02-A03D;

**ENHANCED-POLYMER-INDEXING:** Polymer Index [1.1] 018 ;  
P0000;

Polymer Index [1.2] 018 ;  
ND00; Q9999 Q7158\*R Q7114;

Polymer Index [1.3] 018 ;  
D00 F20 F21 F44 G2948 O\* 6A  
Pb 4A G3270\*R Sn Tr\*R 3A\*R  
4A\*R Ca 2A Mg; D00 F20 Al 3A  
O\* 6A R01544 92; D00 F20 Ti  
4B Tr O\* 6A R01966 686; D00  
F20 O\* 6A Si 4A R01694  
107016; D00 F20 Zn 2B Tr O\*  
6A R01520 866; D00 D67 F21  
H\* Al 3A O\* 6A R02020 129331  
87080; D00 F44 C\* 4A O\* 6A  
Zn 2B Tr R05410 129681; A999  
A102 A077; S9999 S1456\*R;  
A999 A759; A999 A771;

**SECONDARY-ACC-NO:**

**CPI Secondary Accession Numbers:** 2001-191247